Electronic Supplementary Material (ESI) for Physical Chemistry Chemical Physics.

Supplementary Information

Microwave-Gated Dynamic Nuclear Polarization

Aurélien Bornet[a], Arthur Pinon[a], Aditya Jhajharia[b,c], Mathieu Baudin[a,b,c], Xiao Ji[a,b,c], Lyndon Emsley[a], Geoffrey Bodenhausen[b,c], Jan Henrik Ardenkjaer-Larsen[d,e] and Sami Jannin[a,f,g]*

[a] Ecole Polytechnique Fédérale de Lausanne, Institut des Sciences et Ingénierie Chimiques, 1015 Lausanne, Switzerland.

[b] Département de Chimie, Ecole Normale Supérieure, PSL Research University, UPMC Univ Paris 06, CNRS, Laboratoire des Biomolécules (LBM), 24 rue Lhomond, 75005 Paris, France.

[c] Sorbonne Universités, UPMC Univ Paris 06, Ecole Normale Supérieure, CNRS, Laboratoire des Biomolécules (LBM), Paris, France.

[d] Department of Electrical Engineering, Technical University of Denmark, Lyngby 2800, Denmark.

[e] GE Healthcare, Brøndby 2605, Denmark.

[f] Bruker BioSpin AG, Industriestrasse 26, 8117 Fällanden, Switzerland.

[g] Univ Lyon, CNRS, Université Claude Bernard Lyon 1, ENS de Lyon, Institut des Sciences Analytiques, UMR 5280, 5 rue de la Doua, 69100 Villeurbanne, France.

Corresponding Author

* Sami Jannin: sami.jannin@univ-lyon1.fr

Relaxation rate constant

$$R_{1\rho} = \frac{1}{r^6}\frac{1}{15}\left(\frac{\mu_0}{4\pi}\right)^2 \gamma_H^2\left(g_e^2\mu_B^2\right) S(S+1)\left\{\frac{4\tau_{s1}}{1+{\omega_1}^2{\tau_{s1}}^2}+\frac{13\tau_{s2}}{1+{\omega_S}^2{\tau_{s2}}^2}+\frac{3\tau_{s1}}{1+{\omega_I}^2{\tau_{s1}}^2}\right\} \tag{S1}$$

where ω_1, ω_S and ω_I are the nuclear angular nutation frequencies in the rotating frame (in our case $\omega_1/(2\pi)\sim 20$ kHz), the electron angular frequency in the laboratory frame (in our case $\frac{\omega_S}{2\pi}\sim 188$ GHz), and the nuclear frequency in the laboratory frame (in our case $\omega_I/(2\pi)\sim 285$ MHz for ^1H). In the case of isolated electron-nucleus spin pairs in the solid state at low temperature (no rotational or translational diffusion), $\tau_{s1}=T_{1e}$ and $\tau_{s2}=T_{2e}$. However, in our experiment the electron concentration is high (25 mM) which gives rise to electron-electron dipolar couplings on the order of several MHz. Therefore, the apparent transition rate of the electron spin seen by the nuclear spins is not T_{1e} but the flip-flop rate that is close to T_{2e}.

As shown in Figure S1, for all values of τ_{s1} and τ_{s2} in the range of 0.1 μs to 0.1 s, it is the first term in Eq. (S1), i.e., $\frac{4\tau_{s1}}{1+{\omega_1}^2{\tau_{s1}}^2}$ (blue curve in Fig. S1) that dominates over the second and third terms in Eq. (S1) (green and yellow curves in Fig. S1) by at least two orders of magnitude.

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In[135]:= LogLogPlot[{4*t/(1 + (2 π 20 × 10^3 t)), 13*t/(1 + (2 π 188 × 10^9 t)), 3*t/(1 + (2 π 285 × 10^6 t))},
  {t, 10^-7, 0.1}, PlotRange → {{10^-7, 10^-1}, {10^-12, 10^-4}}]
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tracé log log

zone de tracé

Out[135]=

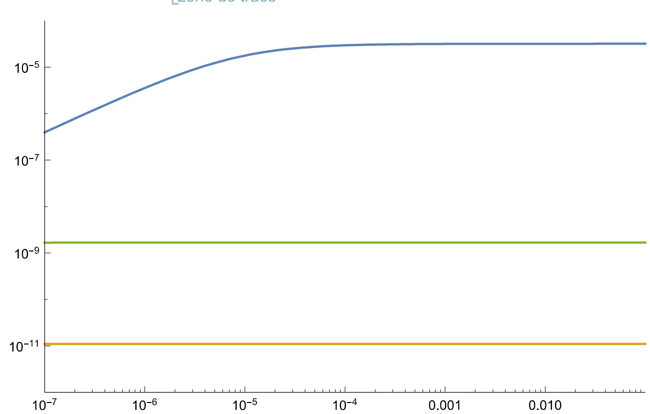

Figure S1

We can therefore simplify equation S1 to:

$$R_{1\rho} = \frac{C}{r^6}\frac{\tau_{s1}}{1 + {\omega_1}^2\,{\tau_{s1}}^2} \tag{S2}$$

with $C = \frac{4}{15}\left(\frac{\mu_0}{4\pi}\right)^2 \gamma_H^2 \left(g_e^2 \mu_B^2\right) S(S+1) = 4.92 \times 10^{-8}$ $\mu m^6 s^{-2}$.

Fitting of cross-polarization curves

A simple stretched exponential can describe the CP build-up as a function of τ_{CP}:

$$I(^{13}C) = 1 - e^{-\left(t/\tau_{CP}\right)^{\beta}} \tag{S2}$$

Numerical fitting yields τ_{CP} = 2.68 ms and β = 0.66.

A similar stretched exponential multiplied by a decaying stretched exponential can describe CP with continuous microwave irradiation,

$$I(^{13}C) = \left(1 - e^{-\left(t/\tau_{CP}\right)^{\beta}}\right) e^{-\left(t/T_{1\rho}\right)^{\gamma}} \tag{S3}$$

Numerical fitting yields τ_{CP} = 2.68 ms, β = 0.66, $T_{1\rho}$ = 7.4 ms and γ = 0.64.